Example: $K_2V_3O_8$

Solution of (3+1)-dimensional incommensurately modulated structure with twinning from single crystal TOF Laue neutron diffraction data.

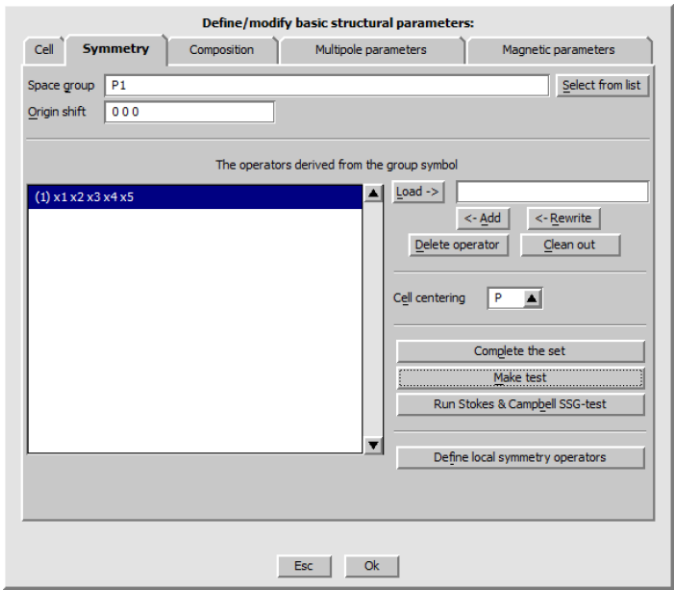
The average structure of $K_2V_3O_8$ is similar to that of fresnoite (JANA2006_Cookbook example 5.4)

Single crystal data were measured on the TOPAZ beamline at ORNL Spallation Neutron Source.

Input files: K2V3O8_Niggli.hkl, K2V3O8_Niggli.mat
Data reduction and Absorption correction: done with software of the diffractometer

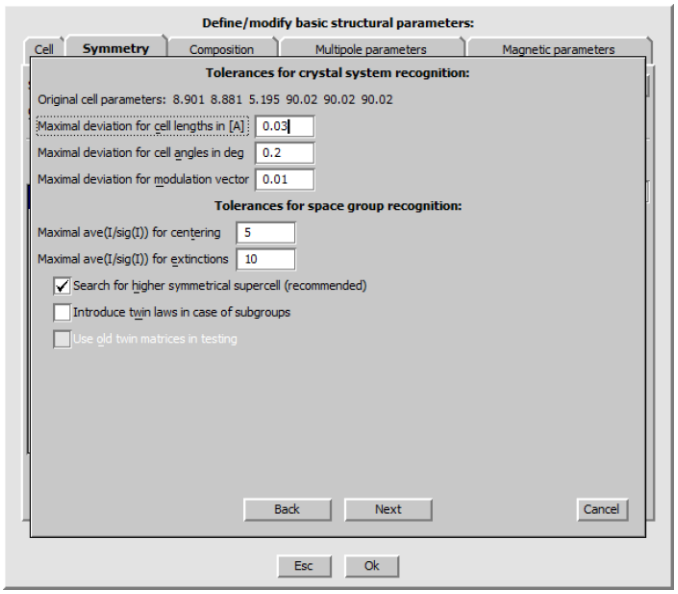
1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager Left pane: locate directory with input files
   Right pane: double-click K2V3O8_Niggli
2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "TOPAZ"; NEXT
   [complete/correct experimental parameters]
   Change the temperature to 90; NEXT Leave all settings unchanged; NEXT
   The program reads 26335 reflections;
   OK; FINISH
   OK; YES to accept the data set
   CANCEL to cancel creating refinement reflection file
3. ***Symmetry Wizard***

Double click EditM50 and select symmetry tab;



The lowest symmetry is use by default. The space group test for single TOF data is skipped in the symmetry wizard as each reflection can be considerably affected by extinction, which is dependent on the actual wave length. Then testing of Laue diffraction symmetry can fail. However, for space group tests based on systematic extinction can still be performed;

OK; Do not rewrite m50; Do not create reflection file;
"File → Reflection file → Make space group test";

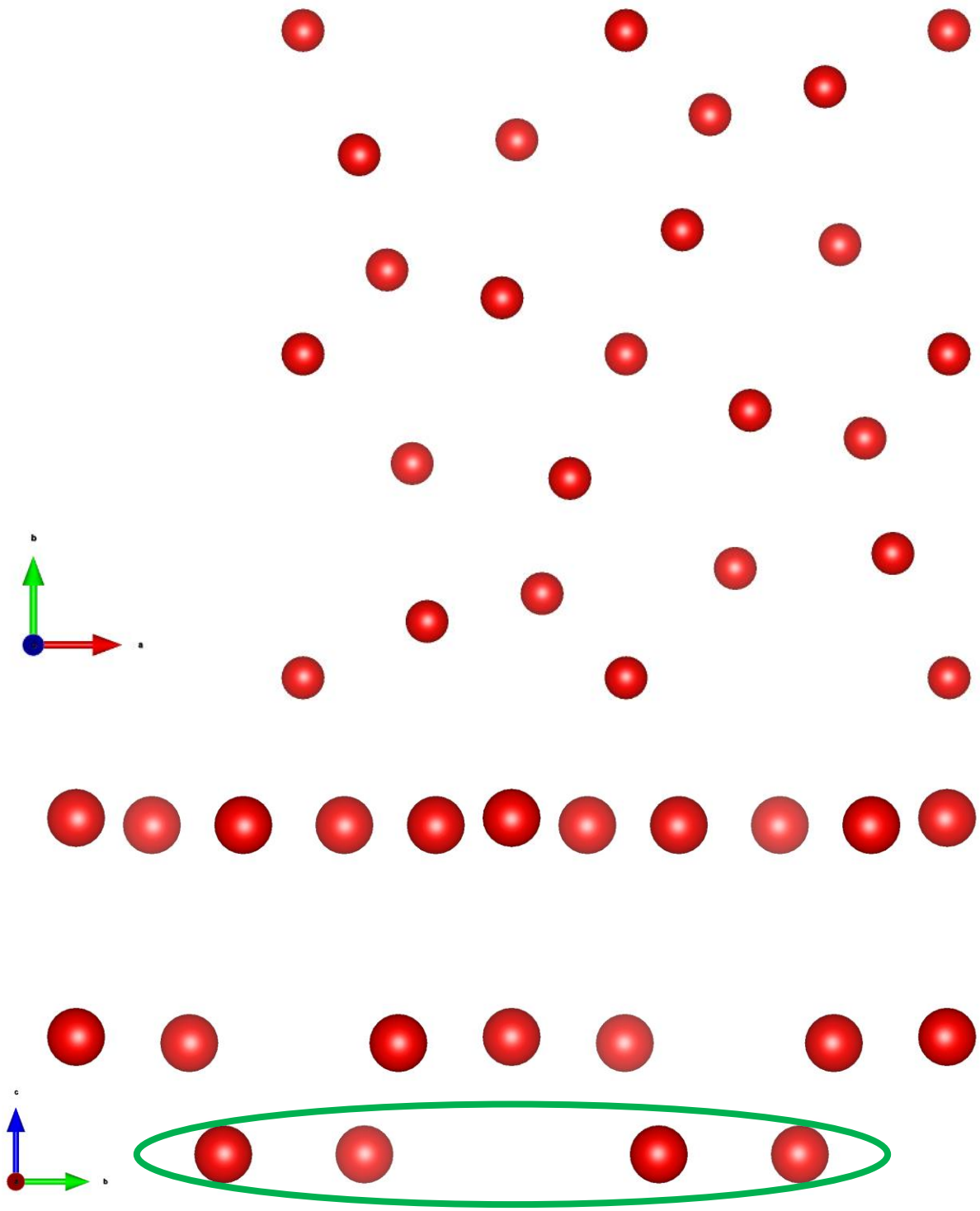


Change "Maximal deviation for cell length in [A]" to 0.03; NEXT
OK; select tetragonal 4/mmm; NEXT
Default select P centering; NEXT
Select P4bm; NEXT

(Several space group symmetries are possible based on the extinction condition and Rint, need other information or several attempts to determine the correct space group symmetry. User can follow example 5.4 to determine the correct space group symmetry for average structure)
FINISH; OK and YES to accept changes

4. ***Creating refinement reflection file***
   YES to start the reflection wizard
   Follow default steps of the reflection wizard
   91/175 reflections discarded due to space group symmetry (some of these reflections are quite strong, indicates the true symmetry might be lower, which will be dealt with later)

5. ***Solution of average structure***
   Start "Tools → Transformation → Go to average 3d structure" For name use "ave_P4bm"
   Follow the steps of the Reflection wizard
   Continue with the new structure
   Start "Run → Solution"
   For Formula type "K V O"
   Rub "Start solution" – rirth mouse double click on the icon;
   Select "Superflip" and "Peaks from Jana2006"
   Select "Use a specific random seed" and type "111" for random seed
   With this option result of charge flipping will be the same in most computers and origin position and special atomic position will be equivalent with this cookbook. For normal work random seed should not be fixed.
   OK
   Superflip converges with R around 23% and confirms the selected space group
   Draw structure shows that all the peaks are assigned with oxygen atoms


b
a
c
b

The four atoms in one layer originated from equivalent positions of O5 atom should be the K atoms, and the V atoms are missing

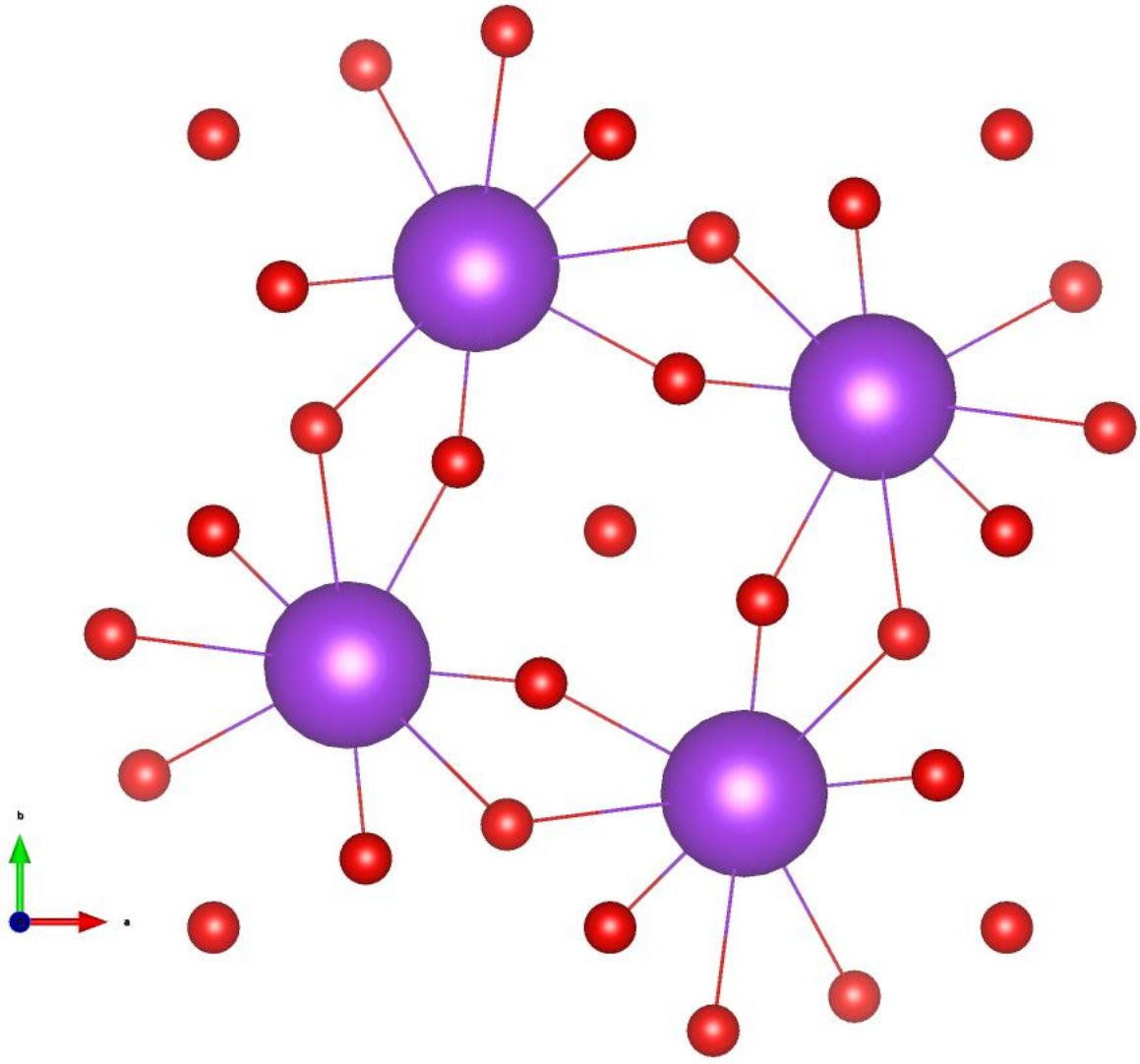
Accept the result

Run “Edit atom” and change O5 to atom the type to K: OK

Select all atoms; Action; Rename selected atoms to “atom_type” + number

Use harmonic ADPs for all five atoms

Draw structure shows the correct position of K atoms



Run Refinements on F(obs)**2 with number of cycles changed to at least 100, skip any warnings that might appear

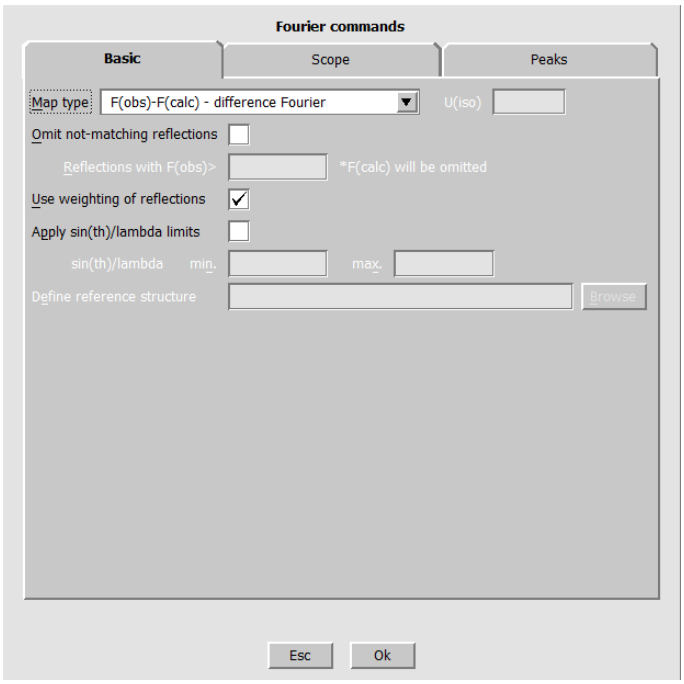
Refinement converges with Robs=7.03%

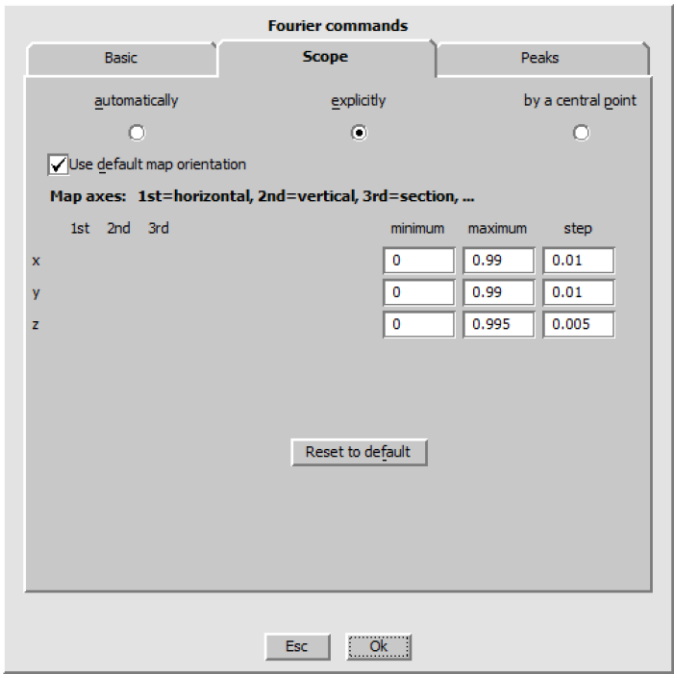
Run difference Fourier with 0.01x0.01x0.005 resolution

We need to find the position of the V atoms using the difference Fourier map

Run Contour;

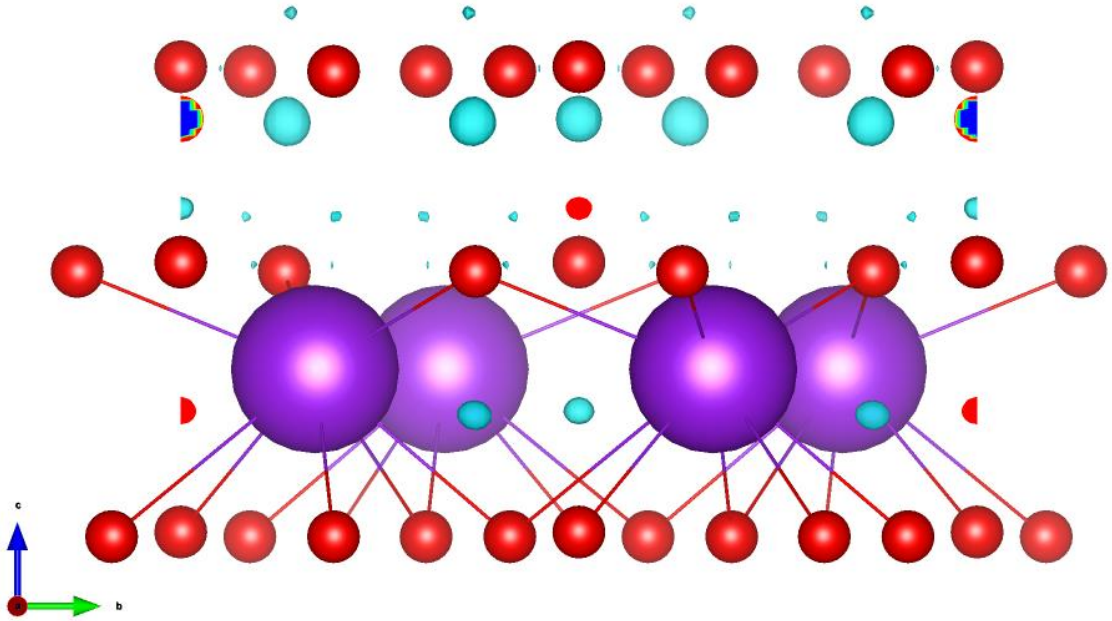
New plot; Options - Fourier map, calculate new ones; draw maps as calculated



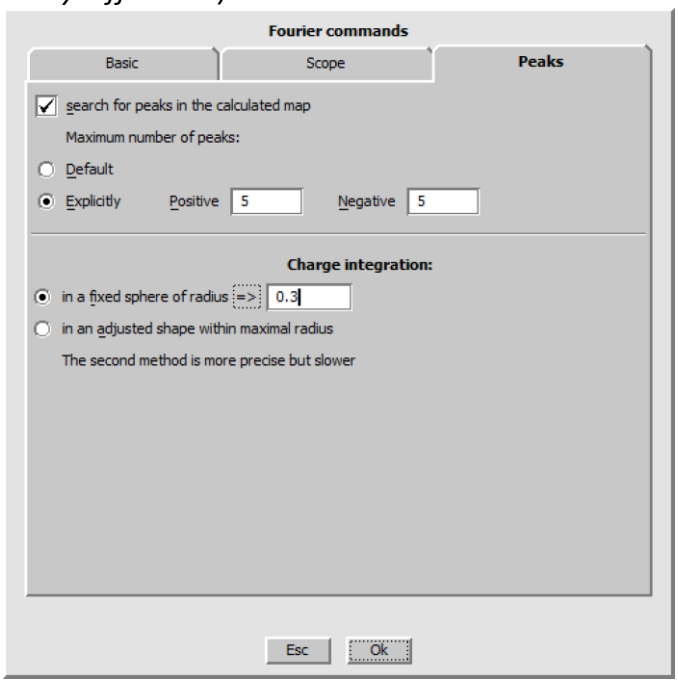


"Run 3d maps" to plot the difference map in 3D, set the isosurfaces level to 1.5 to show only strong peaks.

The large blue spheres are the negative peaks showing the position of V atoms.



Right click Fourier function and open peaks tab, change charge integration sphere radius to 0.3. *(the neutron scatter off the nuclei of the atom, so the sphere radius is much smaller than the electron peak in X-ray diffraction)*



Run Fourier and add difference minima Min1 and Min2 as V atoms.

The scattering length of V is negative, so the minimum peaks are what we should look for

Right click refinement function;

Go to the page “Various” and press button “Fixed command”;

Select “Origin” and fill the atom O2 used for fixing the origin in the polar space group P4bm;

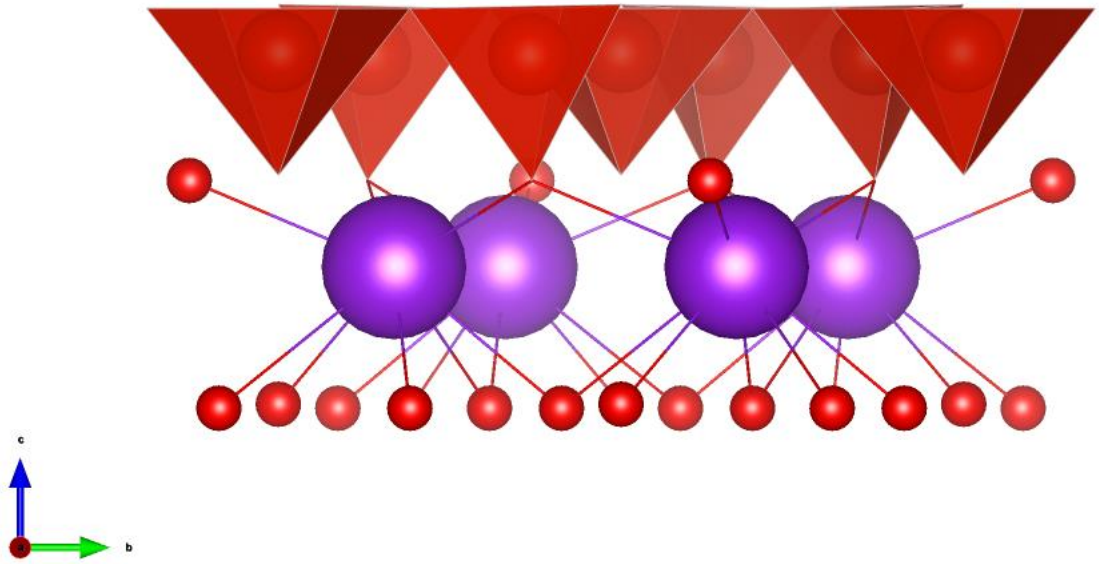
Go to the page “Basic” and modify the dumping factor to 0.2 and enlarge the number of refinement cycles to 100;

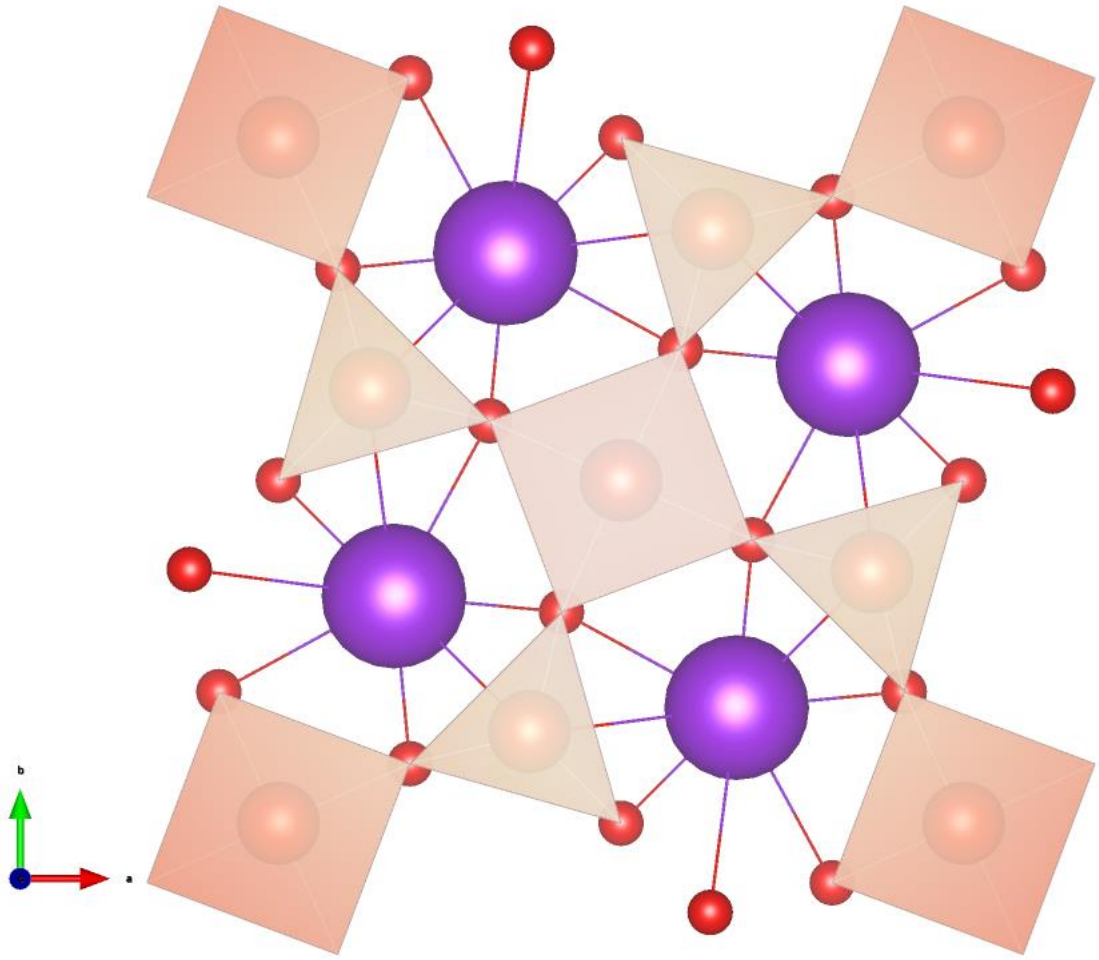
Run Refinement

Refinement converges with Robs=5.74%

In EditM50 check formula: K2 V3 O8 with Z=2

Plot structure to see the final average structure. 2D V tetrahedra and pyramid net work separated by layers of K atoms.





6. ***Back to the modulated structure***

   "File → Structure → Open": open "K2V3O8_Niggli"

   In EditM50 enter formula "K V O" in composition

   "File → Structure → Copy in": import **only** M40 from the average structure "ave_P4bm"

   Fix the origin in analogical way as for the average structure.

   Run refinement on F(obs)**2.

   Refinement confirms R value for the average structure:

```
R factors : [26160=21667+4493/55],   Damping factor:   1.0000
GOF(obs)=  5.71   GOF(all)=  5.30
R(obs)=  21.45     wR2(obs)=  36.55     R(all)=  24.43     wR2(all)=  37.18
R factors for main reflections : [10570=10298+272]
R(obs)=   5.74     wR2(obs)=  13.63     R(all)=   5.92     wR2(all)=  13.69
R factors for satellites +-(1,0) : [15590=11369+4221]
R(obs)=100.00     wR2(obs)=100.00     R(all)=100.00     wR2(all)=100.00
Last wR2(all):
Maximum change/s.u. :   0.0050 for y[O3]
```

7. ***Superspace symmetry***

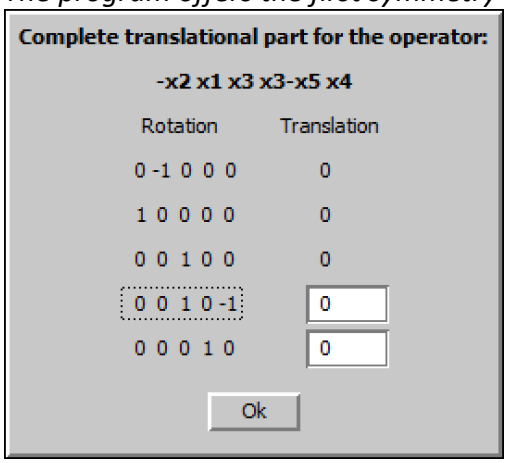
The translation part of the superspace symmetry operators needs to be completed.

Start EditM50

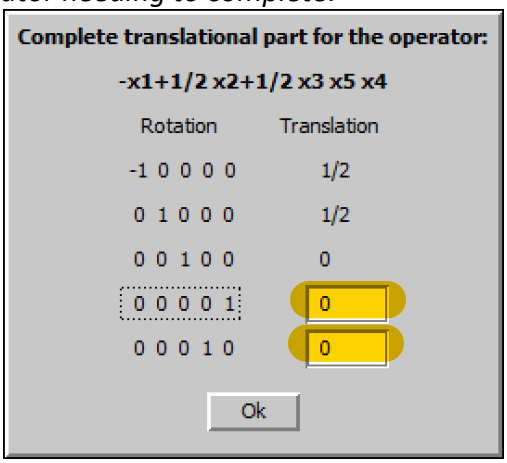
Go to page “Symmetry”

Focus the textbox “Space group” and press TAB.

The program offers the first symmetry operator needing to complete:



and



Change
0
0
to
1/2
1/2

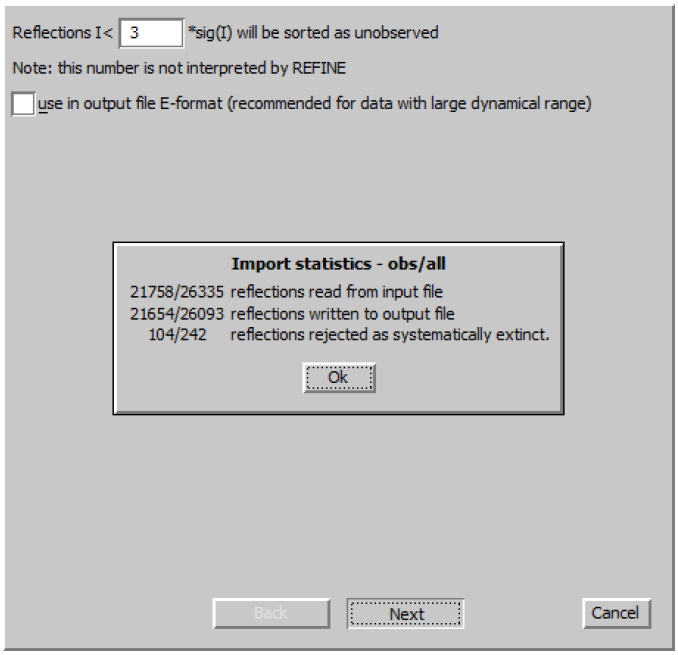
At the first attempt try combination 0 0 for the first operator and ½ 0 for the second one.

The program will not allow it.

Unlike the case of Example 5.4, the number of discarded peaks due to the symmetry are about the same for the two different combinations 0 0 + 0 0 or 0 0 + ½ ½, due to the absence of second order satellite peaks or cross terms, which makes it not useful for determining the correct superspace group. Therefore, both cases need to be tried in the refinement and see which one works. And the same as fresnoite structure, 0 0 + ½ ½ turns out to be the correct combination.

For translation parts use combination 0 0 + ½ ½

Re-create refinement reflection file



8. ***Refinement of modulated structure – position modulation***

Make a copy for modulated structure: "mod_P4bm" to work with

Make sure fix command "fixed origin O2" is present

"Edit atoms": set two position modulation waves for all atoms

This means one harmonic wave along the first wave vector (q1) and one harmonic wave along the second wave vector (q2)

Run refinement

Refinement converges with the following Robs values for all reflections, main reflections and 1st satellites: 6.9%, 5.73%, 12.75%

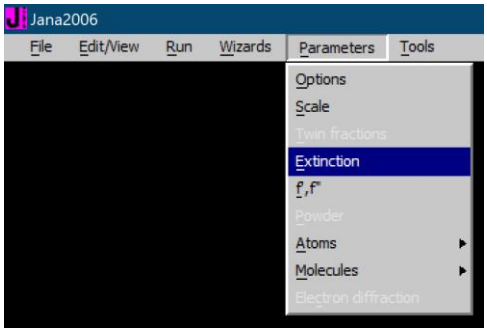
"Edit atoms": add two modulation waves for ADP 2nd on all atoms

Run refinement

Refinement converges with slightly better Robs values: 6.82%, 5.7%, 12.4%. There are warning for negative ADP for V atoms. This can be fixed by fixing the ADP to a reasonable positive value, which won't change the R values much.

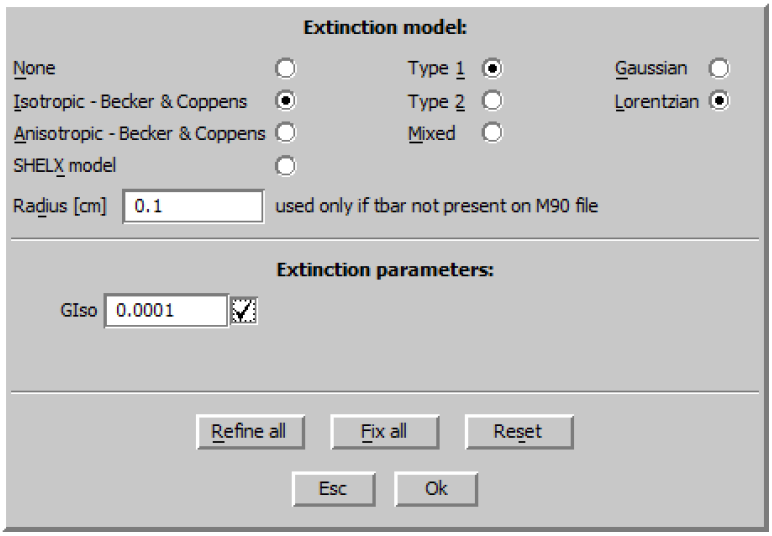
9. ***Extinction correction***

"Parameters → Extinction"

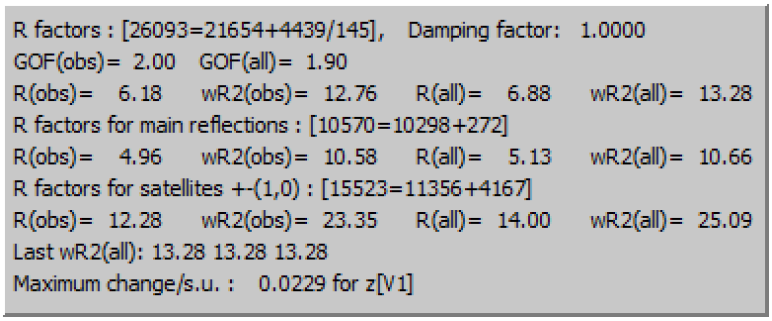


Select "Isotropic-Becker&Coppens" "Type 1" "Lorentzian"

Change Radius [cm] to 0.1 and set the starting GIso to a smaller value, i.e. 0.0001; OK

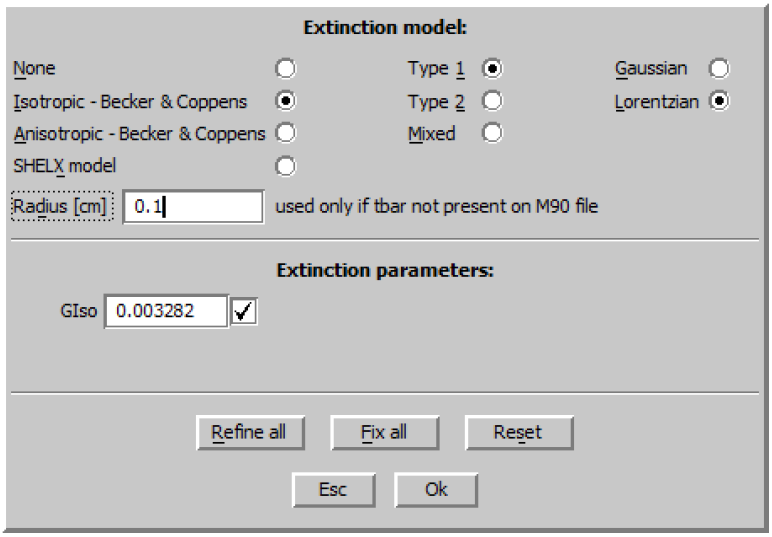


Double-click Refine and refine the structure

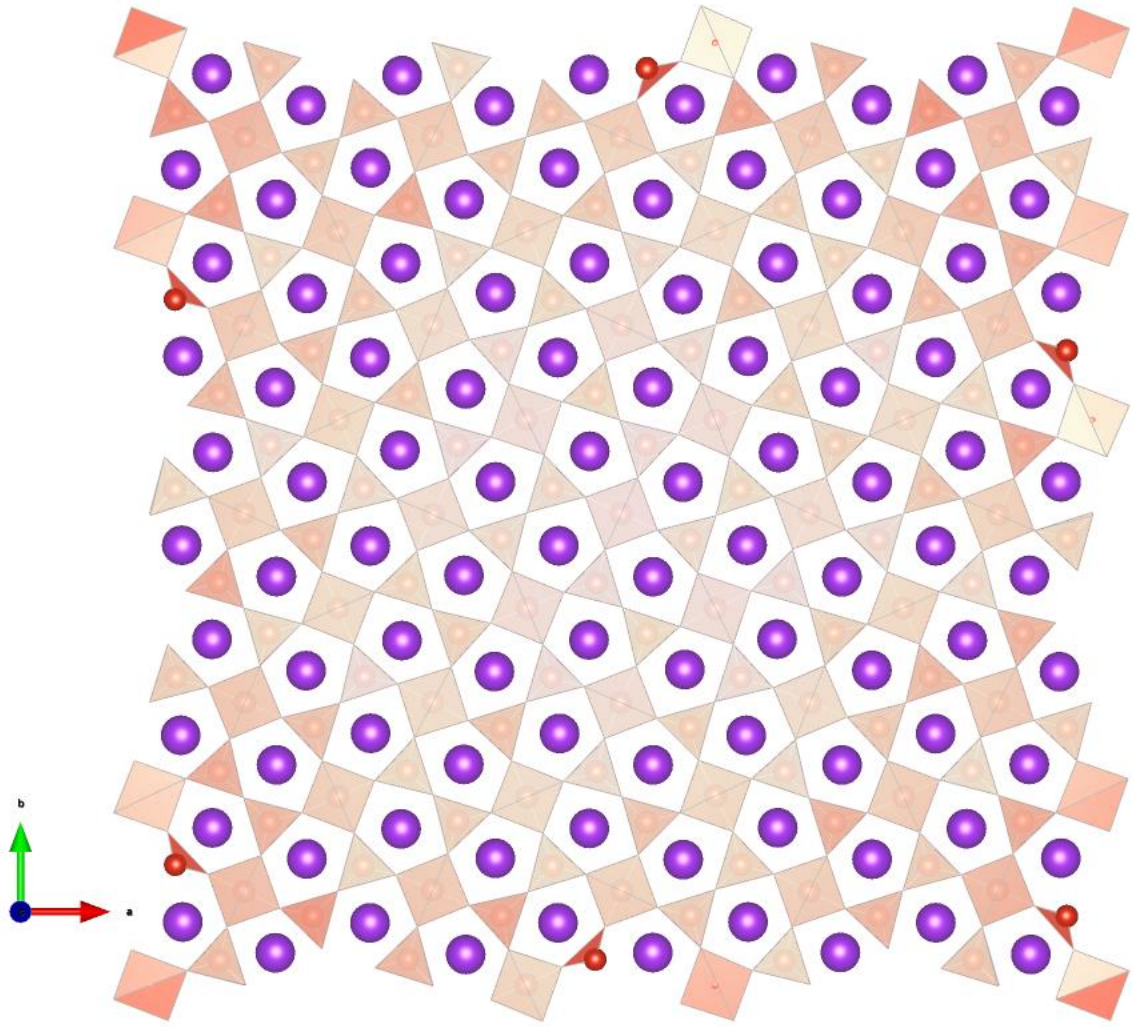


Refinement converges with slightly better Robs values: 6.18%, 4.96%, 12.28%.

Check the extinction coefficient through "Parameters → Extinction"

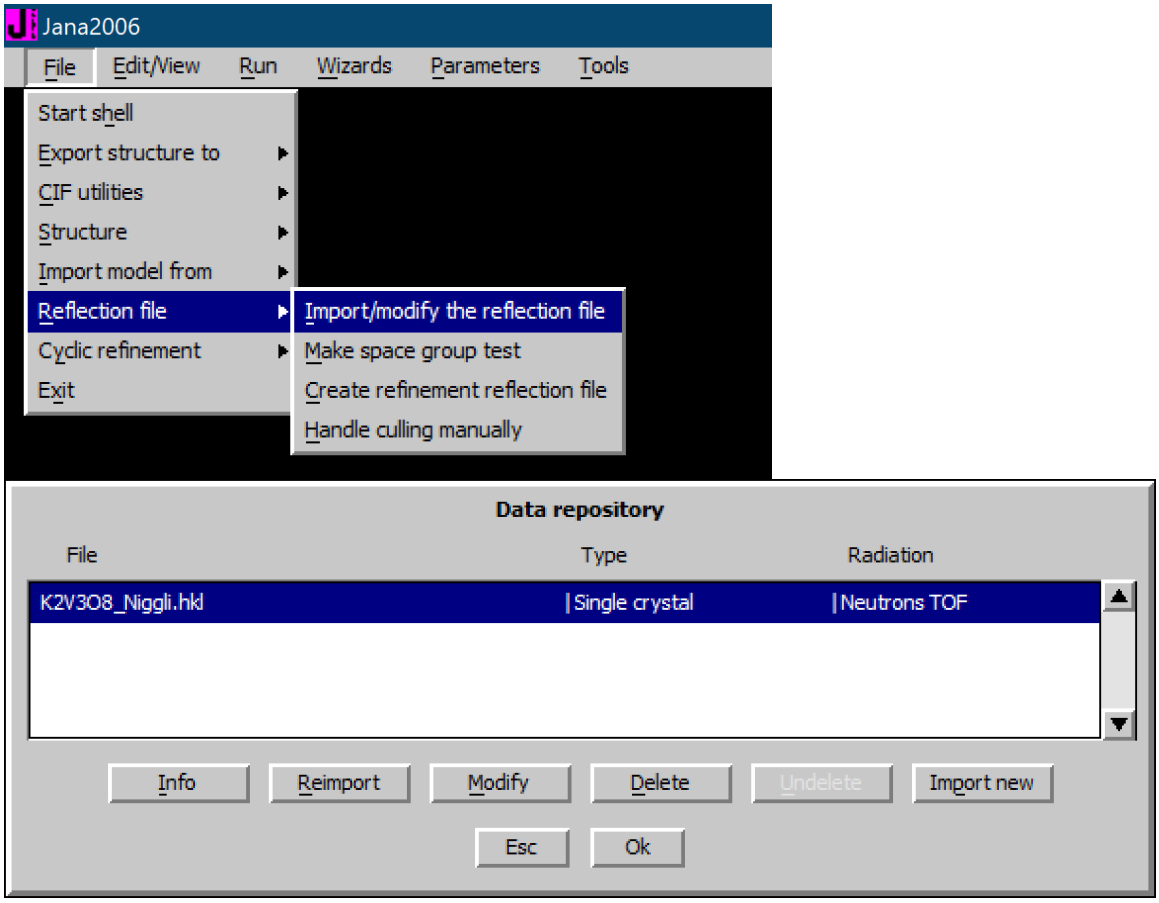


Plot a 5x5x1 super structure. Each individual V polyhedron is not distorted, the framework is modulated by changing the angles between the polyhedra.

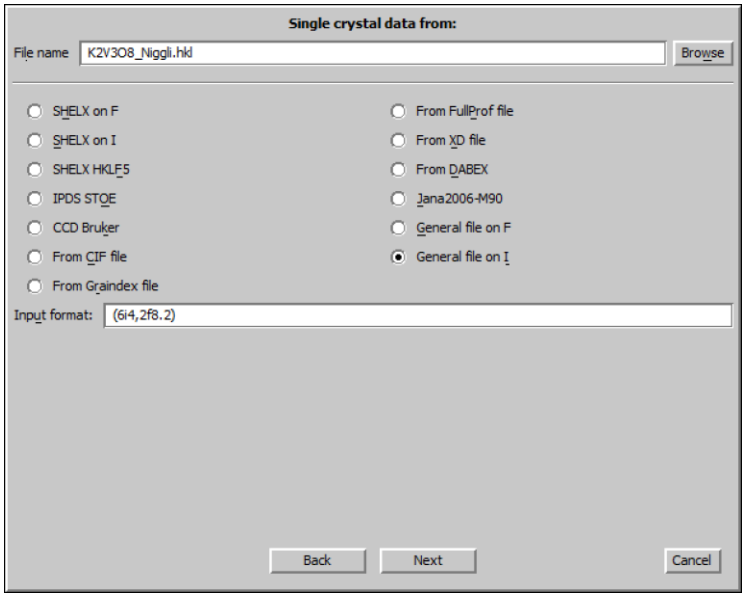


10. Reimport data and create merged refinement reflection file

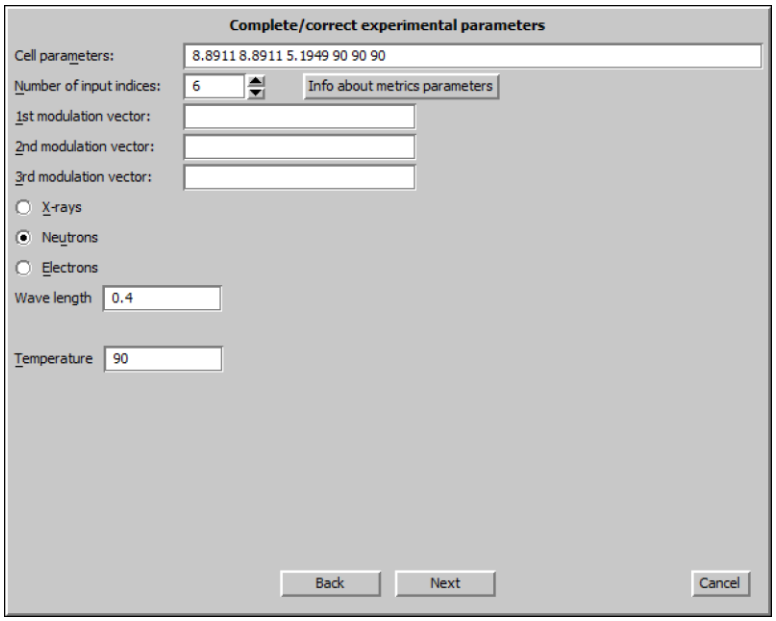
Make new copy for modulated structure: “mod_P4bm_merged” to work with “File → Reflection file → Import/modify the reflection file”:



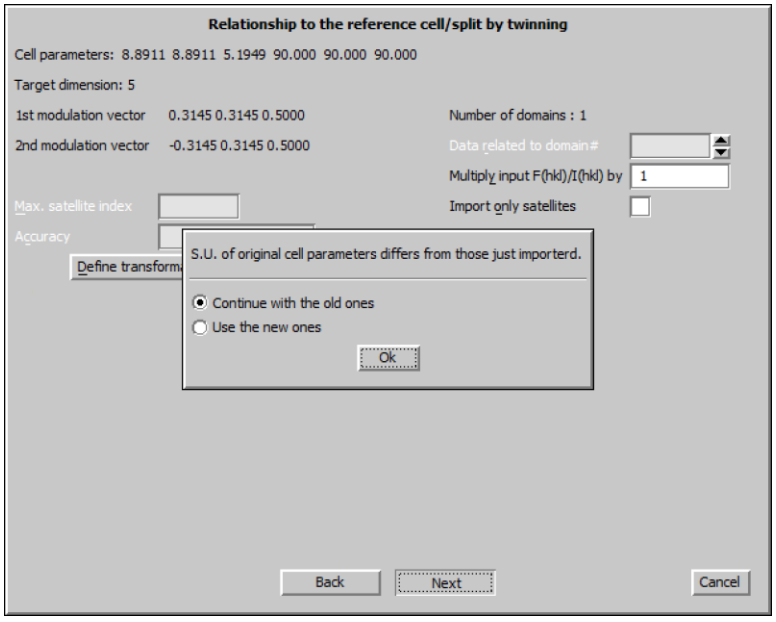
IMPORT NEW
Select “reflection file corrected for LP and absorption”; NEXT
Select “General file on I”, enter file name “K2V3O8_Niggli.hkl”, change Input format to (6i4,2f8.2); NEXT



Select Neutrons and change Wave length to 0.4; NEXT Leave all settings unchanged; NEXT

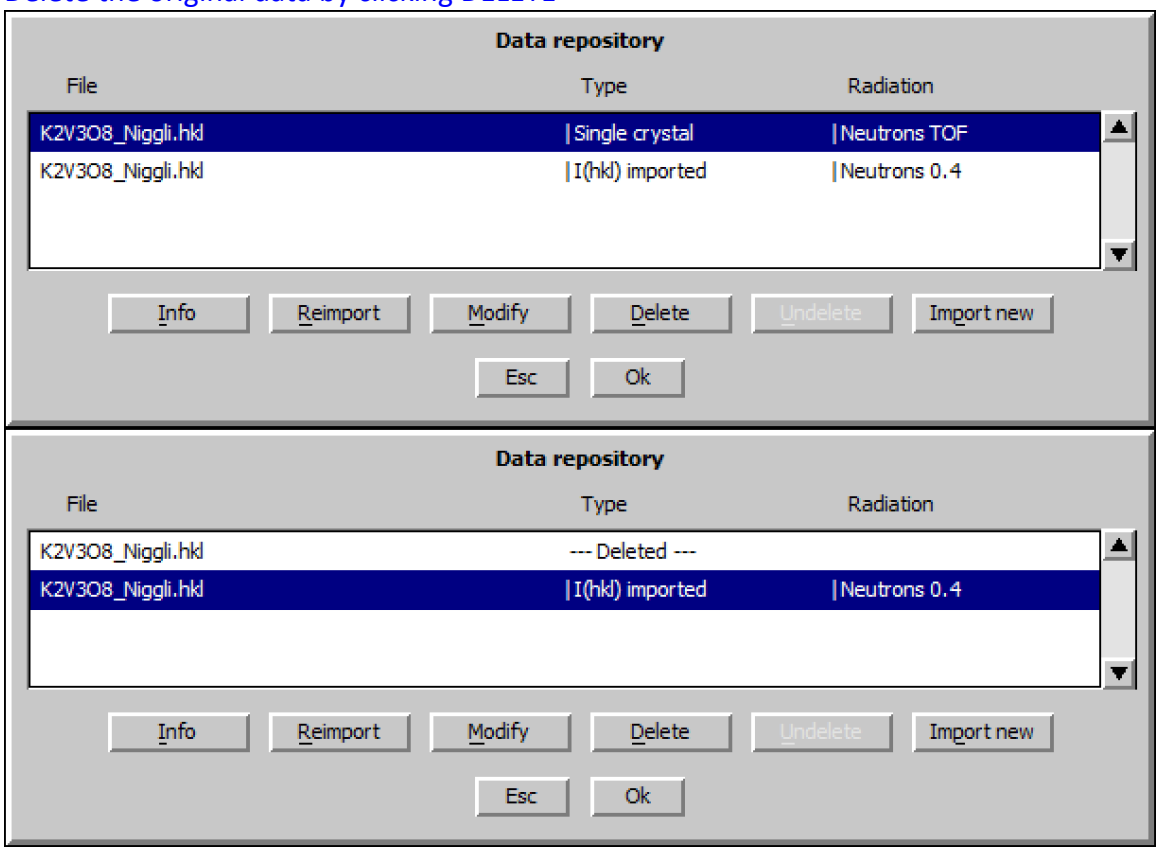


OK to continue with the old ones



The program reads 26335 reflections;
OK; FINISH

Delete the original data by clicking DELETE

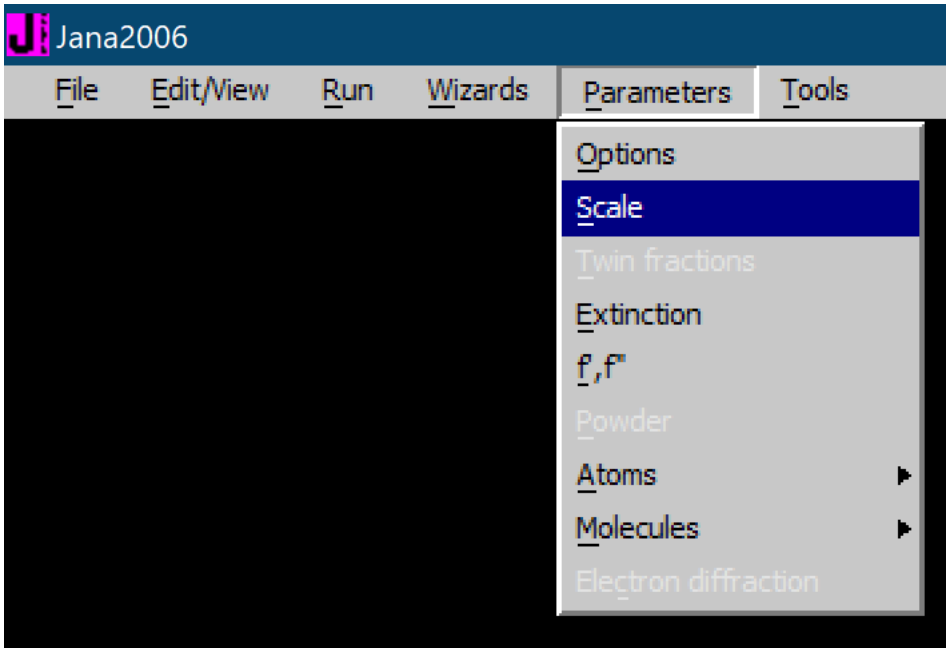


Highlight the newly imported data and OK; YES to accept the data set

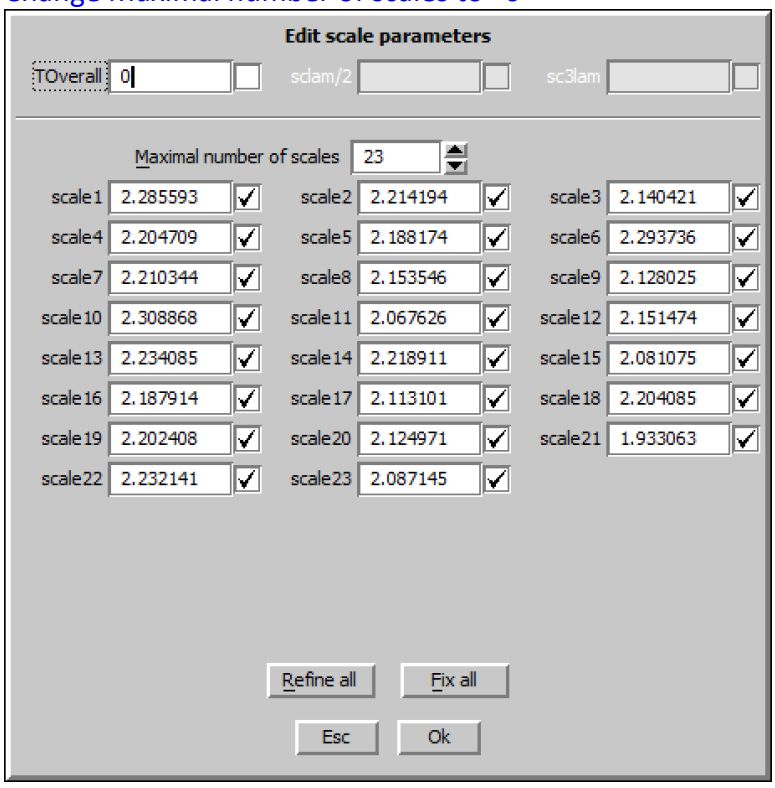
Follow default steps of the reflection wizard

The program discards 242 reflections, 110 observed, Rint=10.23%. This newly imported data merged 21654/26093 reflections to 5488/6034 reflections, which would expedite the refinement process by a lot.

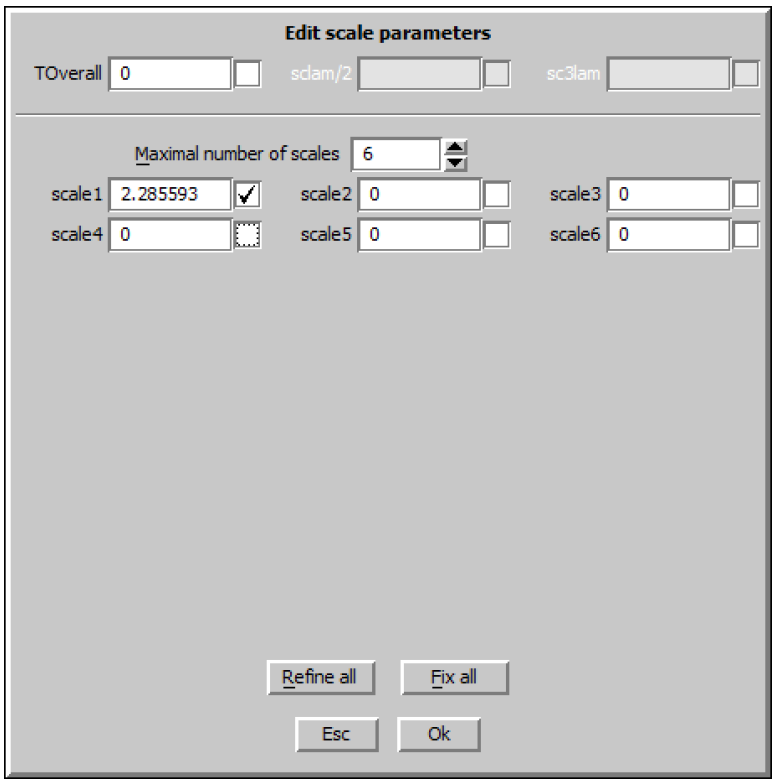
“Parameters → Scale”:



Change Maximal number of scales to “6”



Change all the scales to “0” except scale1, and fix all except scale1 for refinement.



Double-click Refine and refine the structure

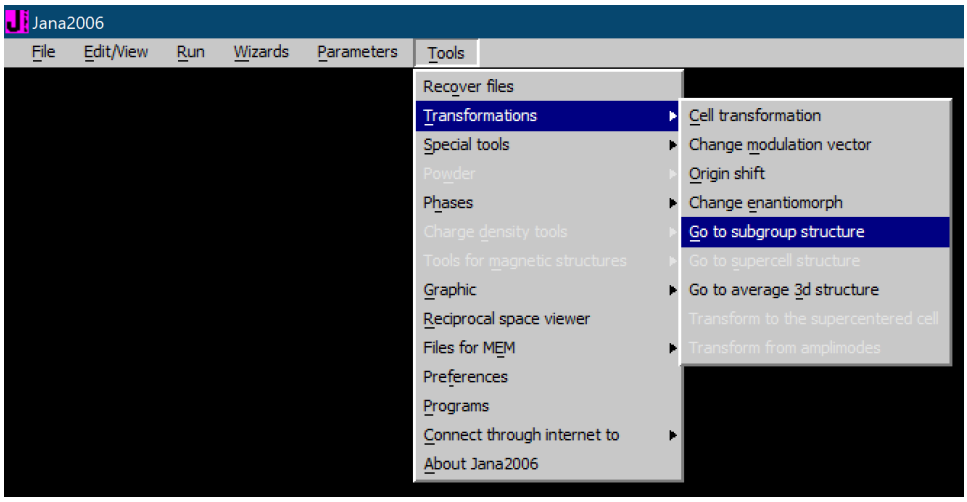
Refinement converges with Robs values: 6.30%, 3.72%, 13.40%.

```
R factors : [6034=5573+461/123],   Damping factor:   1.0000
GOF(obs)=  2.21   GOF(all)=  2.16
R(obs)=   6.30    wR2(obs)=  11.18    R(all)=   6.85    wR2(all)=  11.37
R factors for main reflections : [1798=1783+15]
R(obs)=   3.72    wR2(obs)=   8.07    R(all)=   3.79    wR2(all)=   8.09
R factors for satellites +-(1,0) : [4236=3790+446]
R(obs)=  13.40    wR2(obs)=  19.94    R(all)=  14.64    wR2(all)=  20.45
Last wR2(all): 11.37
Maximum change/s.u. :   0.0182 for xsin1[O2]
```

In most cases where the instrument is well-calibrated, the refinement result should be similar for the merged and unmerged data. However, the extinction correction is dependent on the wavelength which is different for peaks collected from different runs, and merging data from different runs would erase that information. Therefore, the unmerged data is recommended for publication especially for crystals with strong extinction.

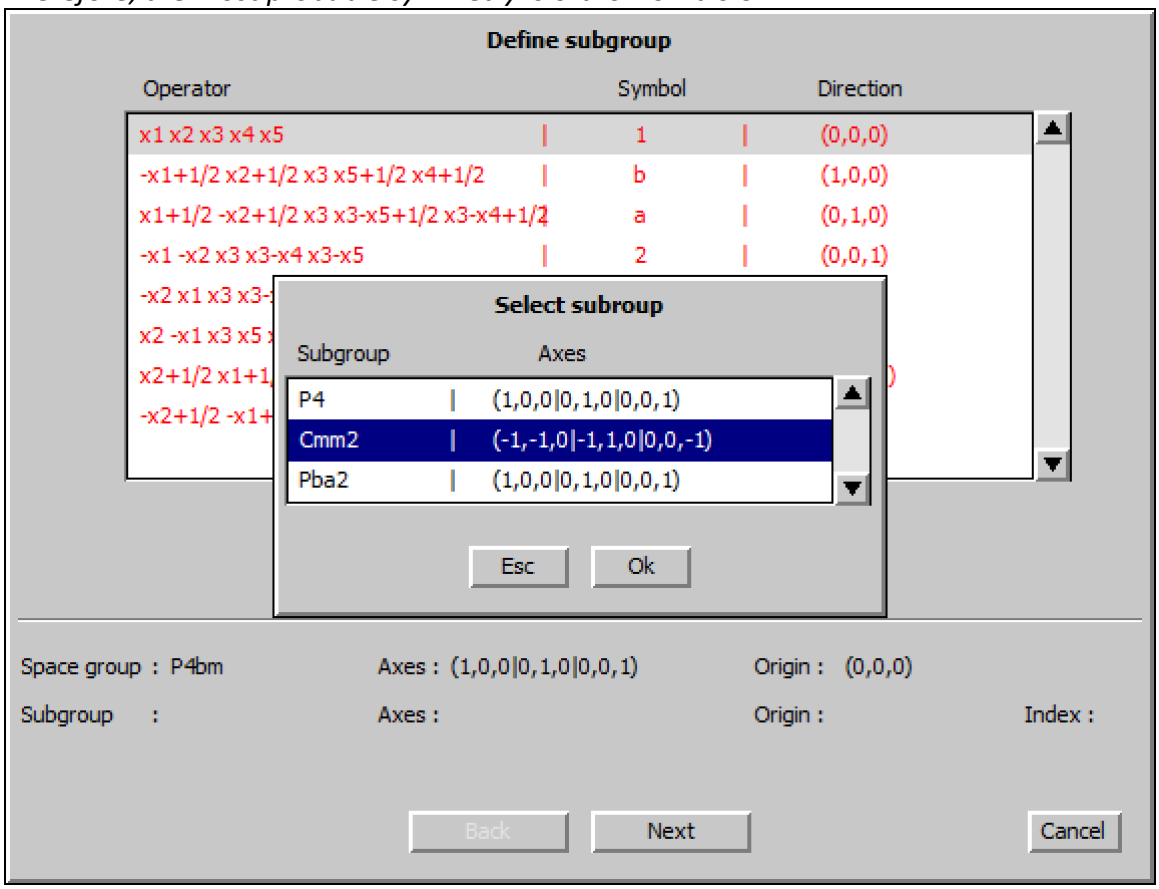
11. *Refinement of modulated structure with subgroup symmetry*

"Tools → Transformations → Go to subgroup structure":



SELECT NON-ISOMORPHIC SUBGROUP; select Cmm2

The discarded peaks are mostly violating the extinction condition of the b-glide plane, so P4 and Cmm2. The average structure shows clear P4bm symmetry, with all the mirror planes present, and the most probable way to break the symmetry is the modulation happens along only one direction, instead of 2. (3+1)d structure for tetragonal structure is only possible when the modulation is along c-axis, which obviously isn't the case in this structure. Therefore, the most probable symmetry is orthorhombic Cmm2.



OK; NEXT; NEXT select the default operator; NEXT

Name the structure “mod_Cmm2_merged”; leave the Make as twinned structure box checked

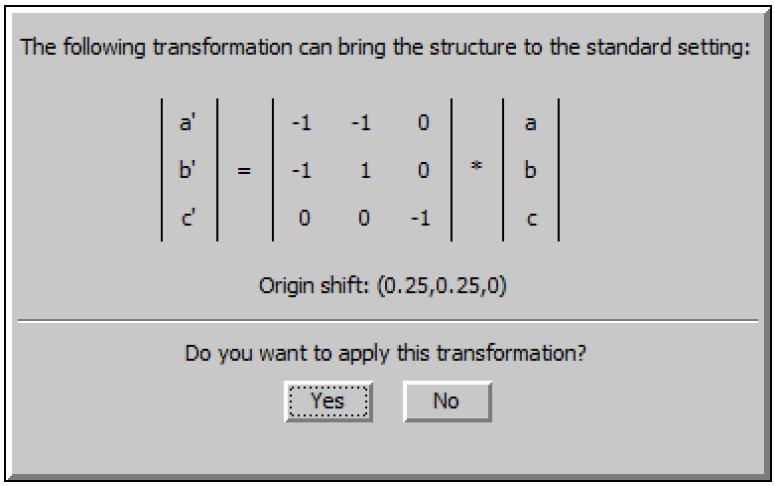
The program will automatically create twin domains with equal volume and have the twin matrix applied.

NEXT; FINISH

Follow default steps of the reflection wizard

Only 16/67 reflections are rejected as systematically extinct for the new space group, all of them are really weak peaks.

Don’t apply the transformation at the end; NO



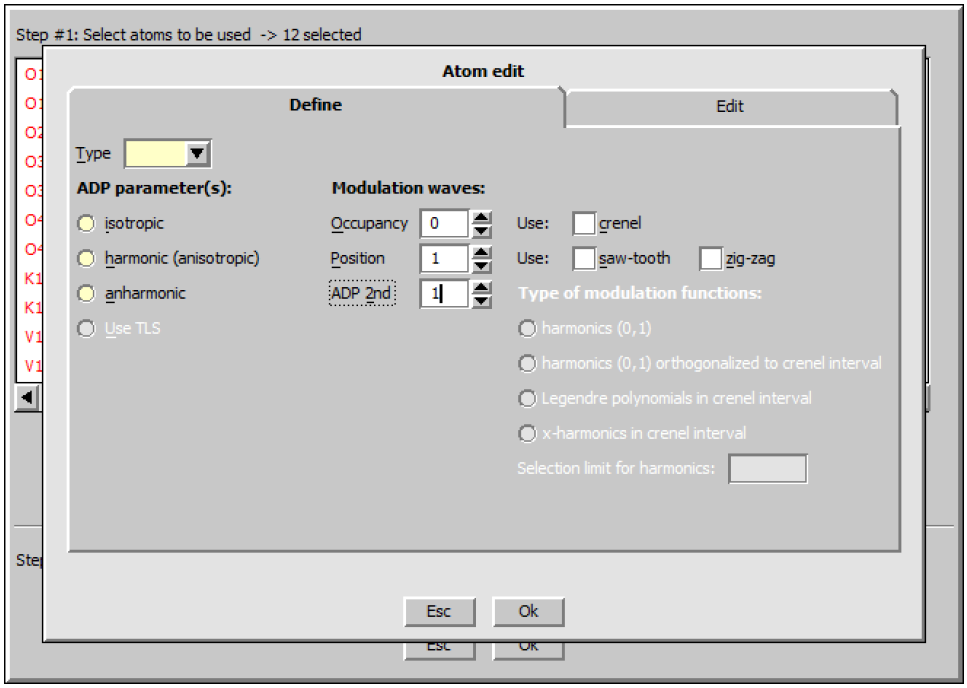
You can transform to the standard setting anytime you want, keep the structure in the primitive setting would allow easy reimportation of the data if you want to refine the structure against the unmerged data

YES to continue with the new structure

Open Edit atoms, SELECT ALL to edit/define atoms

There are 12 atoms now, all but O2 and V2 are duplicated to two sites from the tetragonal structure.

Reduce the number of modulation waves to 1 for both position and ADP 2nd.



OK; OK; YES to accept changes

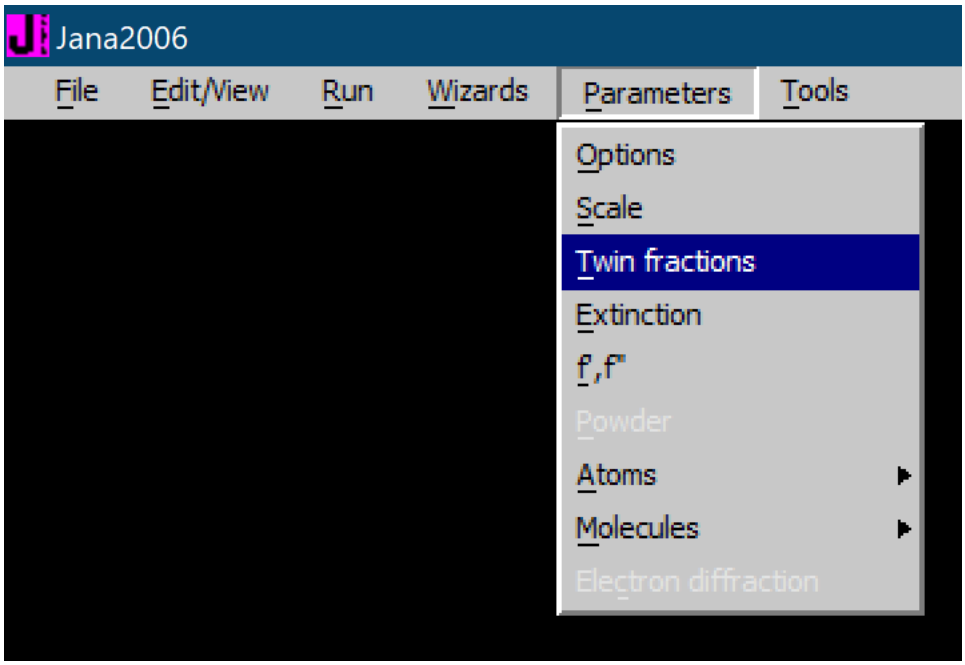
We came from superspace group P4bm(α,α,½)(-α,α,½)0*gg to* Cmm2(β,0,½)0s0(β,½,0)00s*, which is still a (3+2) dimensional superspace group. This is necessary because the data imported is in the form of a (3+2) dimensional structure, even though it could be a (3+1)d structure with 90 degree twinning. By reducing the number of modulation waves to 1, we are only allowing the modulating along one direction to happen, which effectively makes the symmetry to be* Cmm2(β,0,½)0s0*, which is a (3+1)d group. This works pretty easily in this case because only first order satellite peaks are observed in the diffraction pattern. If higher order satellite peaks are observed, we would need to define the 3rd, 4th and higher order modulation waves, and add fix commands to fix all the even order modulation waves to be zero.*

Change the damping factor to 0.5 and start to refine the structure

Refinement converges with Robs values: 6.54%, 4.39%, 13.13%, 12.99%. It may take a long time to reach the convergence criteria, you can end the refinement early when it gets close.

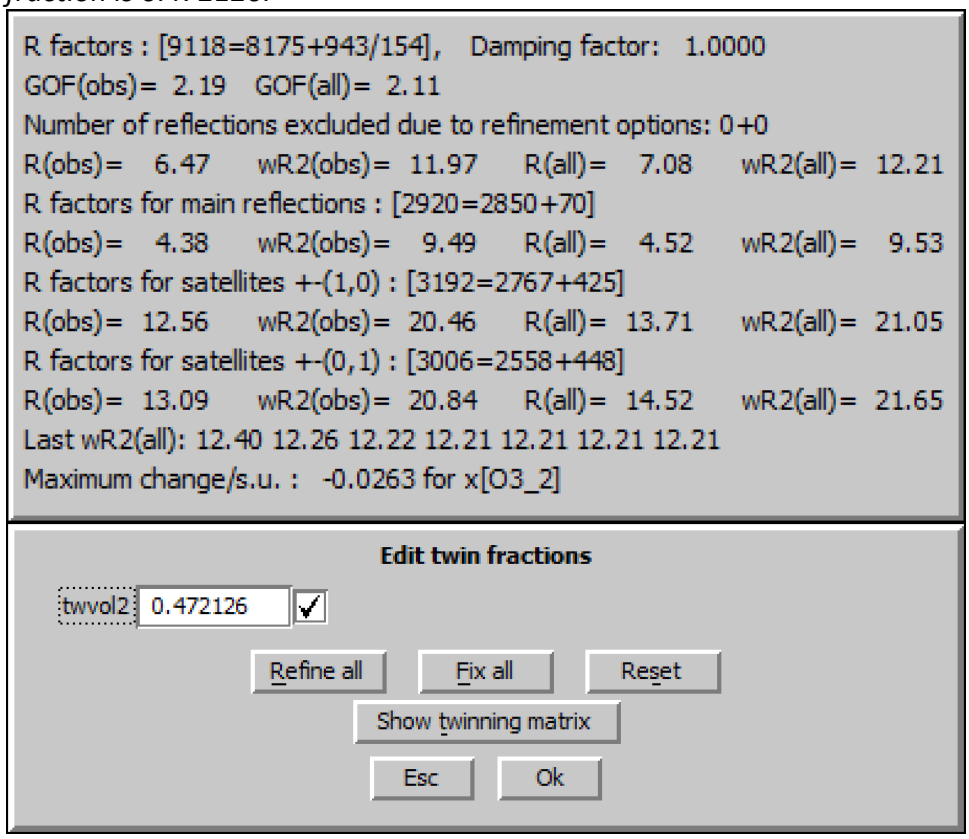
```
R factors : [9118=8175+943/153],   Damping factor:  0.2000
GOF(obs)=  2.22   GOF(all)=  2.15
Number of reflections excluded due to refinement options: 0+0
R(obs)=   6.53     wR2(obs)=  12.15     R(all)=   7.15     wR2(all)=  12.40
R factors for main reflections : [2920=2850+70]
R(obs)=   4.39     wR2(obs)=   9.47     R(all)=   4.53     wR2(all)=   9.52
R factors for satellites +-(1,0) : [3192=2767+425]
R(obs)=  13.13     wR2(obs)=  21.24     R(all)=  14.26     wR2(all)=  21.80
R factors for satellites +-(0,1) : [3006=2558+448]
R(obs)=  12.99     wR2(obs)=  21.48     R(all)=  14.41     wR2(all)=  22.27
Last wR2(all): 12.40 12.40 12.40 12.40 12.40 12.40 12.40 12.40
Maximum change/s.u. :   -1.7353 for z[V2]
```

“Parameters → Twin fractions”; REFINE ALL; OK; YES to accept changes



Double-click Refine and refine the structure with twin fractions turned on

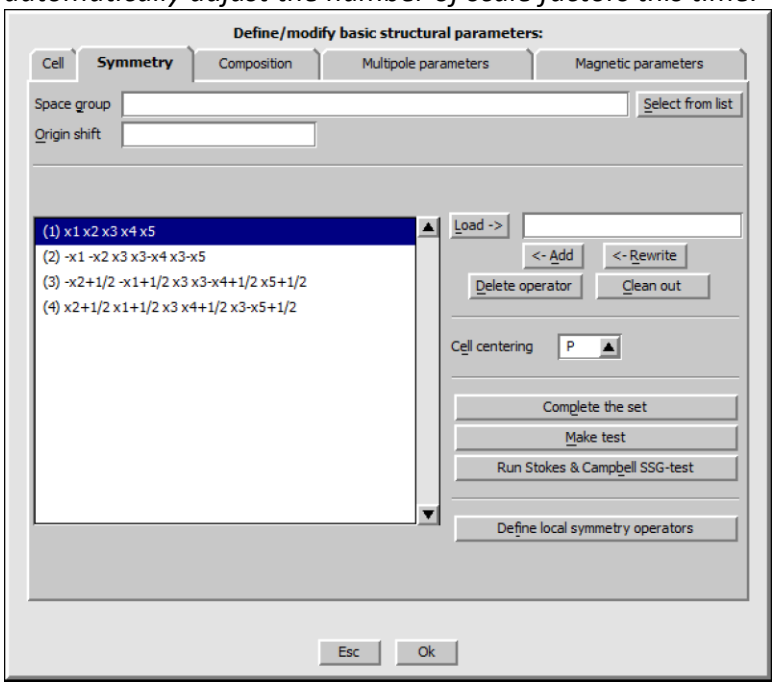
Refinement converges with Robs values: 6.47%, 4.38%, 12.56%, 13.09%. The resulting twin fraction is 0.472126.



Open EditM50 and the symmetry tab

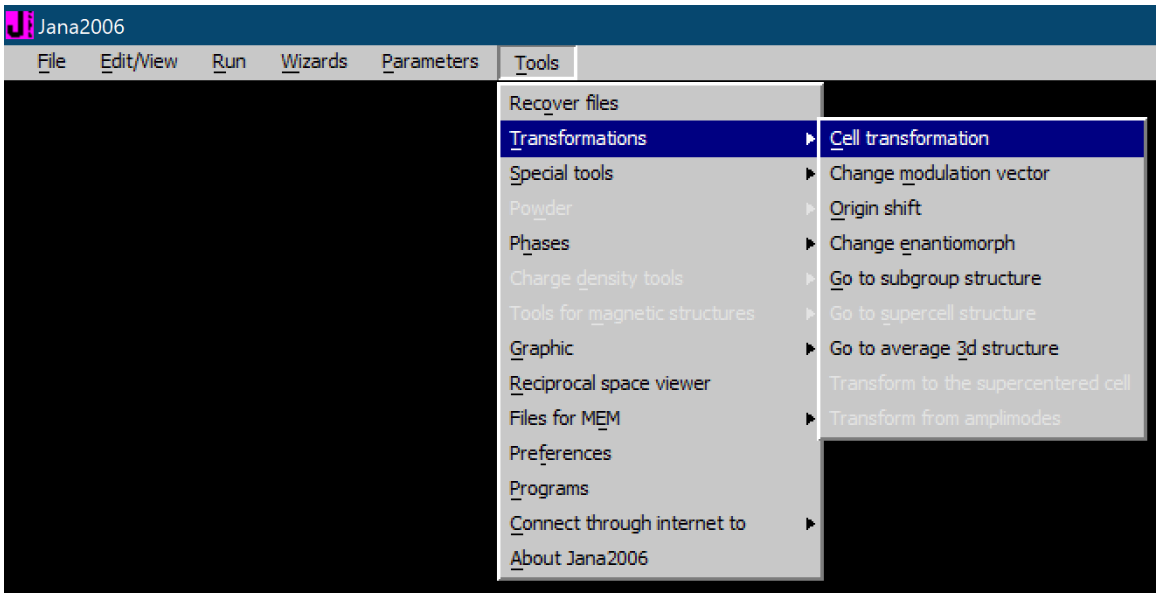
Because the structure is in non-standard setting for space group Cmm2, there is no entry in the space group box, only the symmetry operation listed. We can now reimport the hkl file

as TOPAZ format to refine the structure against the unmerged reflection file, following ***Reimport data and create merged refinement reflection file*** *steps, the program will automatically adjust the number of scale factors this time.*

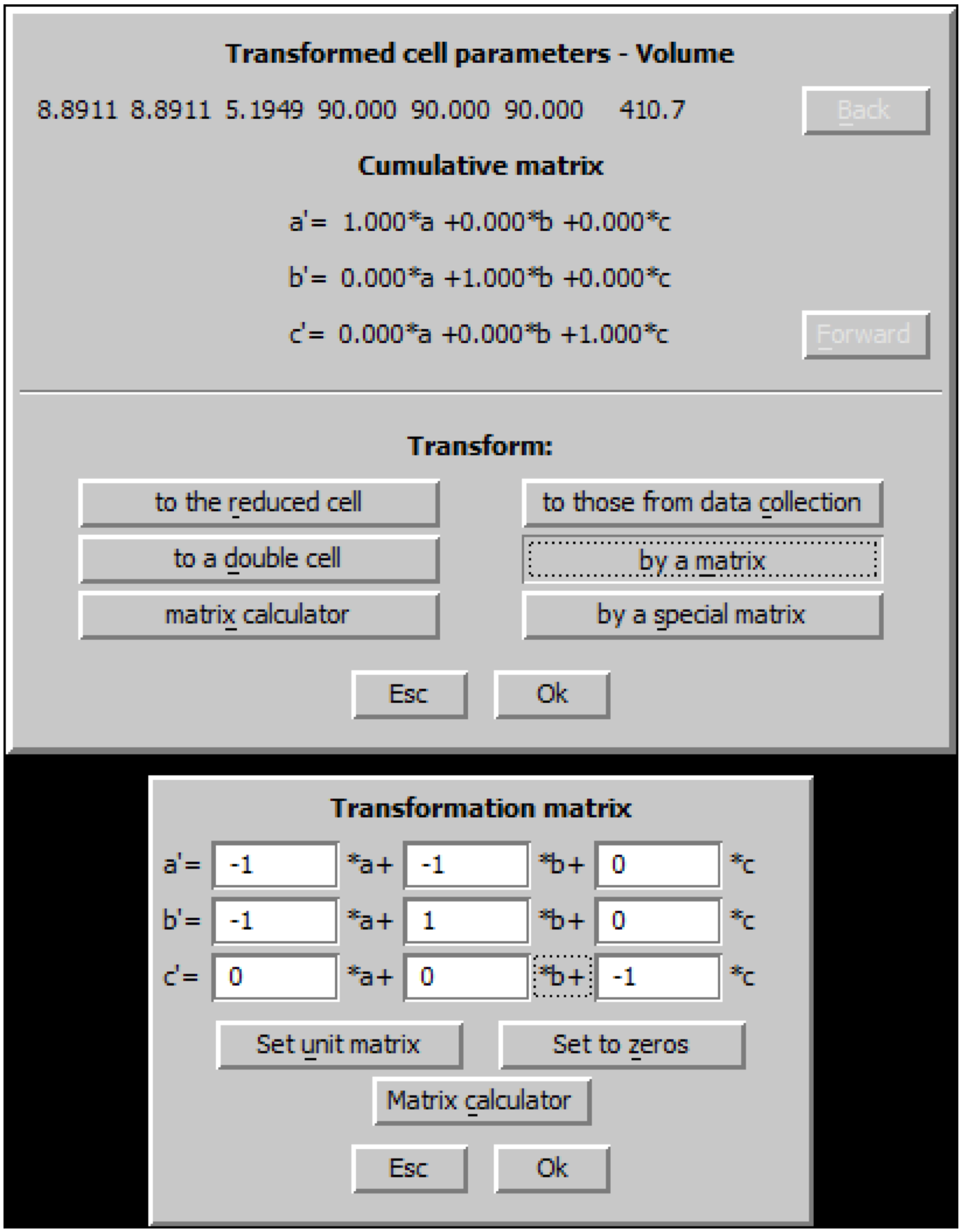


12. Transform the structure to standard orthorhombic setting

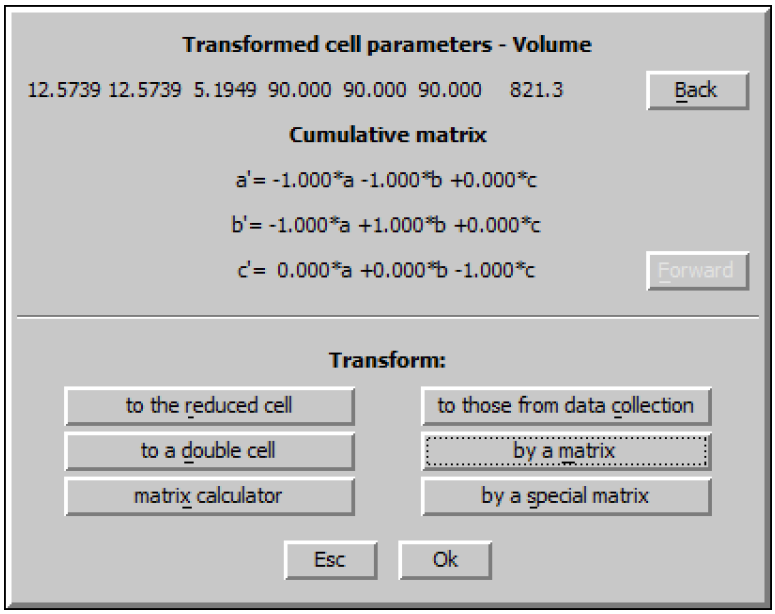
"Tools → Transformations → Cell transformation":



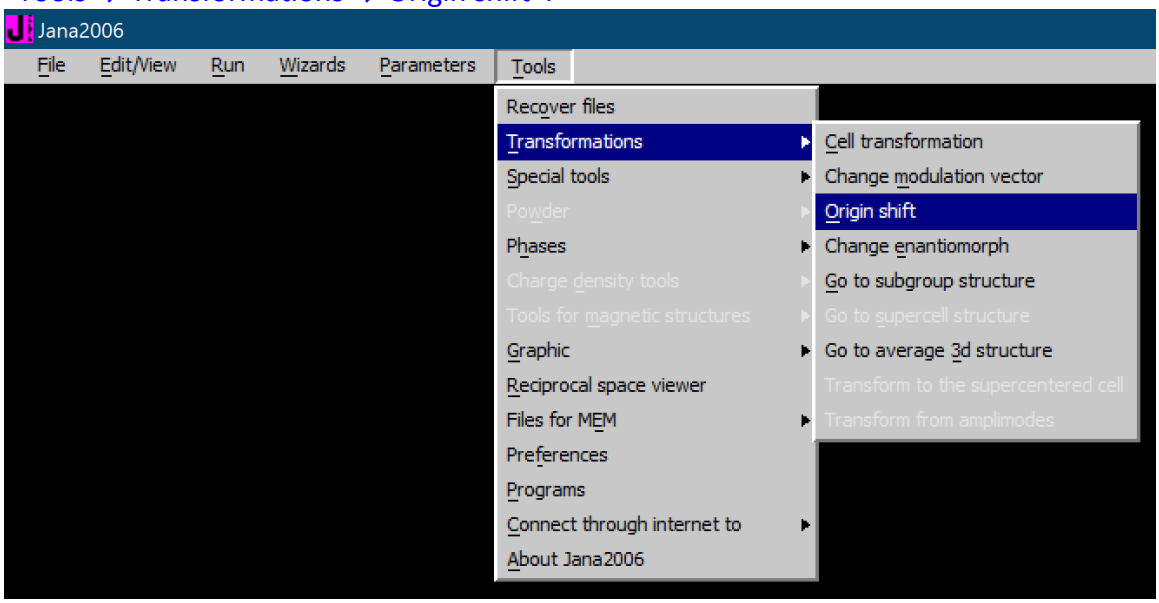
Click BY A MATRIX, enter the transformation matrix shown when we created the subgroup structure.


Transformed cell parameters - Volume
8.8911 8.8911 5.1949 90.000 90.000 90.000 410.7
Back
Cumulative matrix
a'= 1.000*a +0.000*b +0.000*c
b'= 0.000*a +1.000*b +0.000*c
c'= 0.000*a +0.000*b +1.000*c
Forward
Transform:
to the reduced cell
to those from data collection
to a double cell
by a matrix
matrix calculator
by a special matrix
Esc
Ok
Transformation matrix
a'= -1 *a+ -1 *b+ 0 *c
b'= -1 *a+ 1 *b+ 0 *c
c'= 0 *a+ 0 *b+ -1 *c
Set unit matrix
Set to zeros
Matrix calculator
Esc
Ok

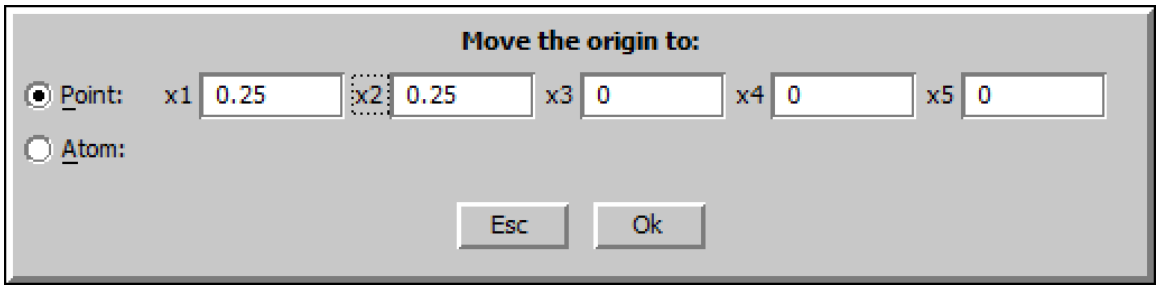
OK; OK



OK to rewrite the old structure.
Follow default steps of the reflection wizard
Open EditM50 and the symmetry tab
The space group box correctly displays Cmm2 with origin shift ¼ ¼ 0
"Tools → Transformations → Origin shift":

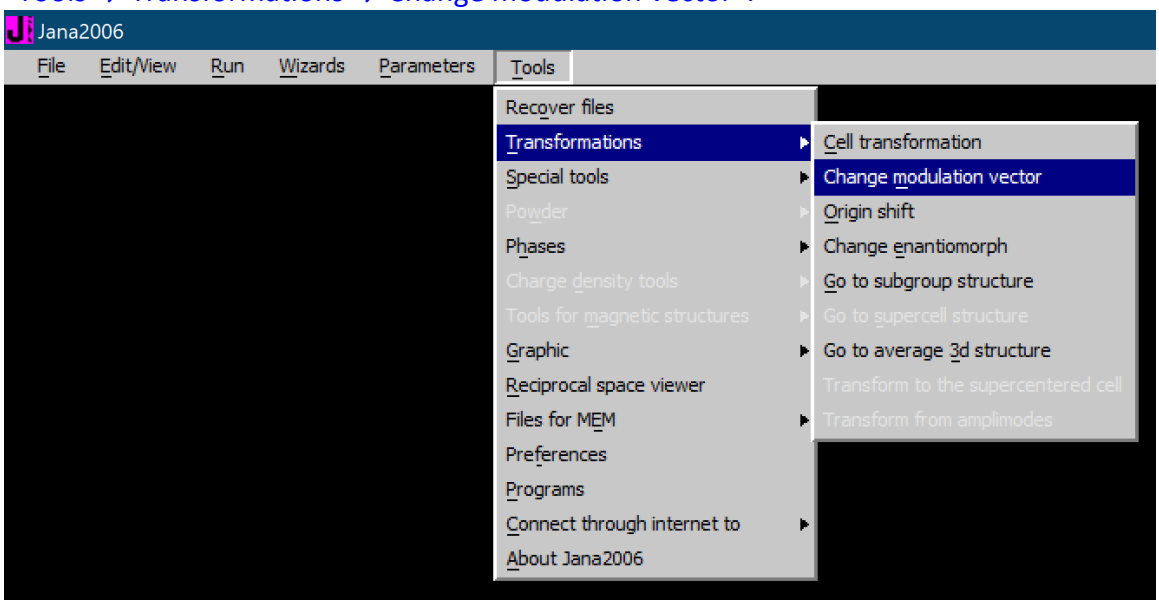


Enter 0.25 for x1 and x2



OK

"Tools → Transformations → Change modulation vector":

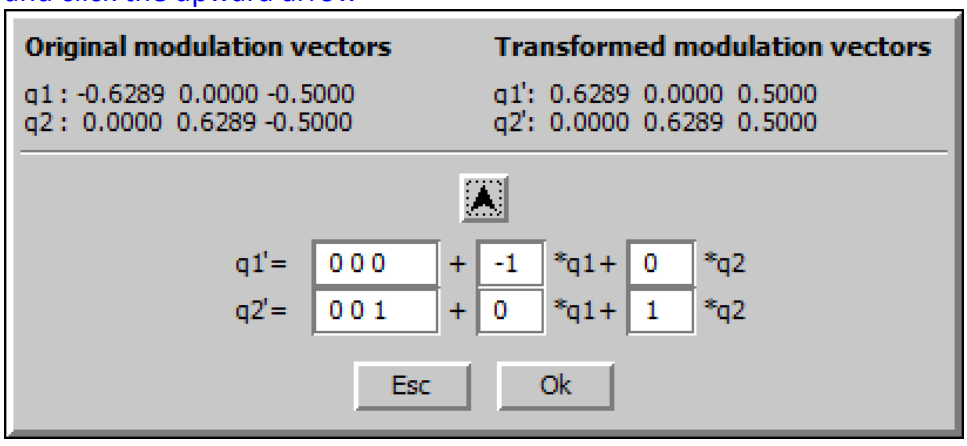


The modulation vectors have negative values now, it's better to change them to positive values.

q1'= (0 0 0) + (-1)*q1 + (0)*q2

q2'= (0 0 1) + (0)*q1 + (1)*q2

and click the upward arrow



Now the transformed modulation vectors are all positive values

OK; OK to rewrite the old structure

Follow default steps of the reflection wizard

The structure is in standard setting of the space group symmetry now.

Double-click Refine and refine the structure

If you are refining against the unmerged data set imported in TOPAZ format, the refinement eventually converges with Robs values: 6.15%, 4.98%, 11.95%, 12.05%.

```
R factors : [26268=21745+4523/176],   Damping factor:  0.1000
GOF(obs)=  1.98   GOF(all)=  1.88
Number of reflections excluded due to refinement options: 0+0
R(obs)=   6.15    wR2(obs)=  12.64    R(all)=   6.86    wR2(all)=  13.17
R factors for main reflections : [10745=10389+356]
R(obs)=   4.98    wR2(obs)=  10.66    R(all)=   5.18    wR2(all)=  10.76
R factors for satellites +-(1,0) : [8050=5961+2089]
R(obs)=  11.95    wR2(obs)=  22.55    R(all)=  13.62    wR2(all)=  24.20
R factors for satellites +-(0,1) : [7473=5395+2078]
R(obs)=  12.05    wR2(obs)=  22.45    R(all)=  13.93    wR2(all)=  24.44
Last wR2(all): 13.18
Maximum change/s.u. :  -4.7513 for z[V2]
```

Plot a 5x1x1 super structure. This structure only have modulation along a-axis and is periodic along b and c-axis.